

Metal Encapsulating Carbon Nanostructures from Oligoalkyne Metal Complexes

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Carbon nanotubes, onions, and related closed-shell carbon particles have commanded extensive recent attention because of their potential applications as unique electronic, magnetic, and mechanically robust materials.¹ When filled with metals,² such nanocapsules have additional promise as magnetic particles, contrasting agents, protecting cloaks, and catalysts and in other applications.^{1,2} Among the various methods for their preparation,¹ the transition metal (especially Fe, Co, and Ni) catalyzed pyrolysis of small organic molecules has shown promise for larger scale production and in structural control.³ While the use of organo-metallic complexes as solid catalyst precursors⁴ or copolyolytic gaseous ingredients^{1g,5} has been reported, all of these studies have been limited to gas-phase experiments at relatively high temperatures. There is very little literature that deals with the organic solid-state generation of carbon nanotubes.^{1a,e,g,6} The latter suffers from extreme conditions, poor yields, or not readily modifiable starting materials. Development of synthetic organic approaches to closed shell large carbon structures is desirable but in its infancy.⁷ Here we present a significant step in its progress.

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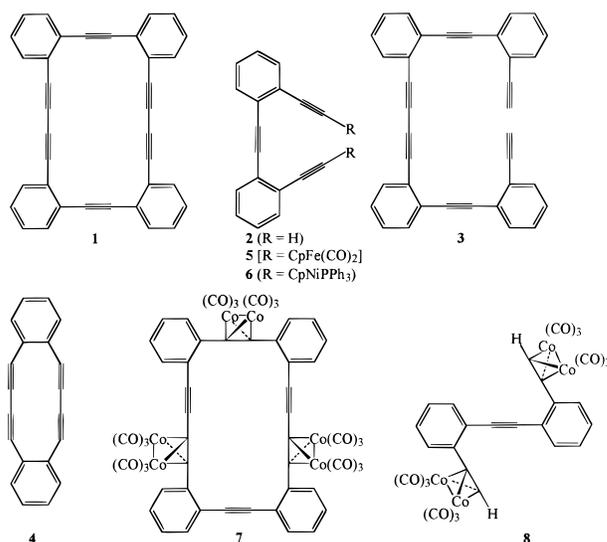
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The impetus for this work derived from the observation that hydrocarbon **1** underwent explosive decomposition at 245 °C to generate CH₄, H₂, and graphitized carbon particles.⁸ While the latter were formed in low yield (1–2% by TEM), in poor quality, and in the presence of mainly graphite and amorphous carbon, it suggested the possibility of a general approach to such carbon allotropes. Initial investigations in this vein were, however, disappointing inasmuch as the less complex analogues of **1**, namely **2**,⁸ **3**,⁹ **4**,¹⁰ (phenylethynyl)-, and ethynylbenzene, while also decomposing explosively on heating with emission of light and gases, did not furnish nanotubes or onions, but only some graphite and mainly amorphous carbon. Annealing the samples in an oven at 800 °C for 6 h increased the graphitized areas, but only marginally. A more detailed investigation of **2**, the “monomeric” precursor to **1**, revealed its explosion point at 141 °C, with a sharp irreversible DSC exotherm ($\Delta H_{\text{rxn}} = -53$ kcal



mol⁻¹),¹¹ and, after heat treatment of the resulting black residue, amorphous, carbon black like structures (TEM).^{1h} Unlike **1**, LDI-TOF MS on thin films of **2** did not provide indications of a measurable oligomerization process.

In contrast, *thermolysis of the complexes 5–8* (for synthetic and X-ray structural details, see Supporting Information) had a *dramatically different outcome*, most strikingly for the cobalt complexes **7** and **8**. In all cases, a relatively smooth reaction commenced below 200 °C, for the carbonyl compounds occurring concomitant with the release of CO gas. For **8**, DSC reveals again a sharp exotherm ($\Delta H_{\text{rxn}} = -47$ kcal mol⁻¹) at 153 °C, followed by a similar endotherm (+71 kcal mol⁻¹) at 188 °C, both irreversible. We believe the former to signal a rapid polymerization process (possibly induced by initial weak¹² Co–Co bond breaking), the latter to reflect the extrusion of (mainly) the CO

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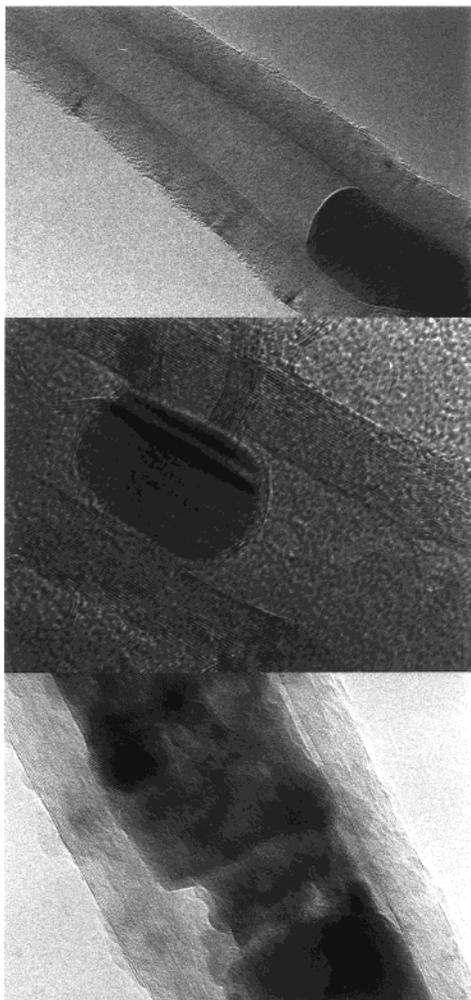


Figure 1. TEM (200 keV, JEOL 200 CX microscope) images of carbon nanotubes containing crystalline cobalt (from **8**; top), iron (from **5**; center), and nickel (from **6**; bottom). The distances between the dark parallel lines of the tube frame correspond to graphitic sheet spacings.

ligands.¹³ Support for this notion is provided by TGA (mass loss at 153 °C corresponding to 12 CO units) and IR spectroscopy (no Co–CO signals). Spectral and GC analysis also showed the evolution of CH₄ and H₂, as observed for **1**,⁸ as well as CO₂ (by disproportionation of CO). The behavior of **7** was qualitatively similar, albeit more complex in detail (DSC). TEM analysis of the pyrolytic powders of **7** and **8** showed that, while graphitization is already clearly visible in the low-temperature regime, thermal treatment (optimal conditions 800 °C, 6 h) produces large quantities¹⁴ of well-formed carbon onions and multiwalled nanotubes, and some graphitic, but very little amorphous carbon. Most of the metal is deposited amorphously in discrete separate patches, as occasional carbon-coated nanorods, or in crystalline (by electron diffraction) form² inside the tubes (and onions), on occasion (but not always) at the tips. Similar conversions, albeit in lower yields (but with larger tube-to-onion ratios), were obtained with the iron and nickel derivatives **5** and **6**, respectively, of **2** (Figure 1). In all cases, the tubes are well graphitized, frequently bent or coiled, made up of 3–50 layers, with inside diameters ranging from 60 to 400 Å and variable lengths up to 50 μm. The carbon spheres vary in size from ~100 to 800 Å. The TEM images are virtually identical with those reported of the same species generated by other techniques.^{1–6} The quality and quantity of these carbon nanoparticles, while not optimal,

(13) Cf., e.g.: Hor, T. S. A.; Chan, H. S. O.; Chiam, C. S. M.; Lim, K. H. *Thermochim. Acta* **1988**, *128*, 175–184.

(14) While this technique is only semiquantitative, TEM analysis of multiple sites and samples suggests “yields” of up to 60%.

constitute a dramatic improvement over those obtained in the pyrolysis of **1**.

It should be stressed that simply mixing **1** or **2** with 5% Co₂(CO)₈ or 10% **8**, or treating **2** with (1) BuLi and (2) NiBr₂, or with CuCl (to generate the alkynyl copper species), or mixing Co₂(CO)₈ with carbon powder and subjecting the resulting mixtures to the above conditions gave soots with very little graphitization, whereas ethynylbenzene–Co₂(CO)₆ and **3**–[Co₂(CO)₆]₂ resulted in graphite and amorphous material. Thus, while metal complexation is clearly essential, there appears to be pronounced specificity with respect to precursor structure, suggesting perhaps the necessity for certain molecular or packing features conducive to closed shell carbon construction. If these could be delineated, the prospect for a tailored synthetic strategy might be realized.

The present work raises some interesting questions with respect to the mechanism of the present nanoparticle assembly.^{1,15} While it is noteworthy that a metalated polyyn growth model of single wall nanotubes has been proposed,^{15c} more prevalent, particularly in explanations of conventional multiwalled particle assembly, is the suggestion that (pyrolytic) carbon is dissolved in catalytic metal particles from which it is extruded in regular form.¹ It is possible that such, too, is the case starting with **5**–**8** and that the frequency, distribution, and activity of the catalytic sites depends on the structure, composition, and morphology of the starting complex.¹⁶ If so, it appears reasonable to postulate that the oligoyn framework undergoes radical initiated and/or metal mediated trans- and intermolecular oligomerization¹⁷ to some (pre)graphitic network that is subsequently annealed¹⁸ to closed shell carbon particles.¹⁹ Be that as it may, the current conversion of molecularly defined, high-energy, high C/H ratio metal complexed hydrocarbons to encapsulating tubes and spheres is novel, amenable to structural variation,²⁰ and relatively tractable mechanistically, at least in its initial phases, perhaps leading to an alternative to existing methods.

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Supporting Information Available: Experimental and spectral details of the syntheses of **5**–**8** and X-ray structural data for **5**, **7**, and **8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>. JA9924602

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